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DL capacitance–emission spectroscopy of determining the electrochemical behavior of anodized aluminum in aqueous solutions

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Abstract

In the present investigation, holographic interferometry was utilized for the first time to determine the rate change of the double layer (DL) capacitance of aluminum samples during the initial stage of anodization processes in aqueous solution without any physical contact. In fact, because the DL capacitance values in this investigation were obtained by holographic interferometry, electromagnetic method rather than electronic method, the abrupt rate change of the DL capacitance was called DL capacitance–emission spectroscopy. The anodization process (oxidation) of the aluminum samples was carried out chemically in different sulfuric acid concentrations (0.5–3.125% H_2SO_4) at room temperature. In the mean time, the real-time holographic interferometry was used to determine the difference of the DL capacitance of two subsequent values, dC, as a function of the elapsed time of the experiment for the aluminum samples in 0.5%, 1.0%, 1.5%, and 3.125% H_2SO_4 solutions. The DL capacitance–emission spectra of the present investigation represent a detailed picture of not only the rate change of the DL capacitance throughout the anodization processes, but also, the spectra represent the rate change of the growth of the oxide films on the aluminum samples in different solutions. Consequently, holographic interferometry is found very useful for surface-finish industries especially for monitoring the early stage of anodization processes of metals, in which the rate change of DL capacitance of the aluminum samples can be determined in situ.

Keywords: Holographic interferometry; Alternating current impedance; Anodization process; Double layer capacitance; He Ne laser light

1. Introduction

In recent works conducted by the author [1–16], an optical transducer was developed for materials testing and evaluation of different electrochemical phenomena. The optical transducer was developed based on incorporating methods of holographic interferometry for measuring microscopic deformations and electrochemical techniques for determining electrochemical parameters of samples in aqueous solutions. In addition, the optical transducer was applied not only as an electrometer for measuring different electrochemical parameters but also, the optical transducer was applied as a 3D-interferometric microscope for detecting different micro-alterations at a metal surface in aqueous solution, at a microscopic scale. Initially, the optical transducer was used to determine the mechanochemical behaviors of metals in aqueous solution, i.e., stress corrosion cracking, corrosion fatigue, and hydrogen embrittlement [1–5]. Determinations of the mechanochemical behaviors of metals in aqueous solutions, was based on detecting

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micro-deformations and measuring the corresponding current density by the optical transducer. Further more, the optical transducer was applied as an optical corrosion-meter [6–8] for measuring cathodic deposit and anodic dissolution layers of metals in aqueous solutions. Also, the optical corrosion-meter was utilized to determine the cathodic and anodic current densities which correspond to the cathodic deposit and anodic dissolution layers, respectively. The cathodic and anodic current densities were measured electromagnetically by the optical transducer, rather than electronically by one of the classical methods, i.e., an Ammeter, of measuring the flow of the electronic current in a conductor. In addition, the optical transducer was applied to measure uniform corrosion and localized corrosion on metal surfaces and on substrates covered by organic coatings or under crevice assemblies [8–14]. The optical transducer was also used to document adsorption and desorption phenomena of chemical species on metal surfaces in aqueous solutions[12]. Finally, the optical transducer was applied as an electrometer for measuring the double layer capacitance, the alternating current impedance and the corresponding oxide layer thickness of metals in aqueous solution [15,16].

The objective of the present work was to detect an emission spectroscopy of the DL capacitance of anodized films of aluminum samples as a function of time in sulfuric acid solutions by using holographic interferometry. More specifically, holographic interferometry was used not only as a 3D-interferometric microscope for monitoring the anodization of the aluminum samples, but also holographic interferometry was utilized for the first time as a DL capacitance spectrometer for determining the rate change of the DL capacitance of oxide films of the aluminum samples in aqueous solution. The reason for the selection of aluminum samples for this investigation, because aluminum is known to readily anodize, oxidize, not only by electrochemical methods but also by only a chemical oxidation [17]. In other words, a thicker oxide layer than the layer which the aluminum normally has in air can form by either electrochemical or chemical methods. In this study, normal chemical oxidation was applied in order to produce a thicker oxide layer than the layer which the aluminum normally has in air. Also, by detecting the emission spectroscopy of the DL capacitance of the aluminum samples, one can determine the electrochemical behavior of the oxide film of the aluminum directly without physical contact.

2. Theoretical analysis

In a mathematical relationship derived by the author elsewhere [15,16], one can measure the DL capacitance of the oxide film on a metal sample by holographic interferometry as follows:

$$1/C = Z = L/(ee^{\circ}A), \tag{1}$$

where C is the double layer capacitance of the oxide film, Z is AC impedance of the oxide film, e is dielectric constant, 8.4 of aluminum oxide, Al_2O_3, e° is permittivity of the free space, 8.85×10^{-14} Farad/cm, A is area of the sample, L is thickness of the oxide film which can be obtained by holographic interferometry [7], where

$$L = U = \frac{N\lambda}{(\sin\alpha + \sin\beta)}, \tag{2}$$

where N is the number of fringes, λ is the wavelength of the laser light used in the experiment, α and β are the illumination and the viewing angles, respectively. Both α and β angles can be obtained from the setup of the experiment.

Eq. (1) describes the relationship between the DL capacitance and the AC impedance of the oxide film to the thickness of the film. In other words, one can measure the DL capacitance as well as the AC impedance by knowing the thickness of the oxide film. Since the thickness of the oxide film can be measured by holographic interferometry from Eq. (2), Eq. (1) can be applied to measure the DL capacitance as well as the AC impedance of the aluminum oxide of aluminum samples during anodization, oxidation, process of the aluminum in sulfuric acid solutions.

By applying Eq. (1), one can detect the emission spectroscopy of the DL capacitance of an oxide film on a metal surface in aqueous solution by holographic interferometry. This can be achieved by plotting dC versus the elapsed time of the experiment, where dC is the difference between DL capacitance of two subsequent values. By plotting dC versus time, this will definitely reflect the abrupt rate change, emission spectroscopy, of the DL capacitance values as a function of time.

3. Experimental work

Metallic samples of pure aluminum (99.7%) were used in this investigation. The aluminum samples were fabricated in a cylindrical form with dimensions of 8 cm diameter and 0.15 cm thickness. Then, all samples were polished and ground by silicon carbide papers until the finest grade is reached. In order to be sure that the aluminum samples have attained scratch-free surface, the samples were etched by a chemical solution for 2 min at a temperature range of 85–95 °C. The etching solution is made of 3 g/L of sodium hydroxide + 30 g/L of trisodium phosphate. At the beginning of each test, the aluminum sample was first immersed in the acid solution. Then a hologram of the sample was recorded using an off-axis holography, see Fig. 1 for the optical